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BASE OIL FOR WELL-BORE FLUIDS

The present invention relates to base oils for use in well-bore fluids, such as drilling fluids, to well-bore fluids incorporating the base oil and to the use of such fluids.

Well-bore fluids, for example drilling fluids, are used in oil and gas recovery and in geothermal energy and mineral exploration and extraction operations. The fluid serves a number a functions including removal of drilled cuttings from the bore-hole and sealing of the well-bore surfaces so that fluid loss into the formation being drilled is minimised. The fluid also lubricates and cools the drill pipe during the drilling operation.

Oil based drilling fluids have been used for around 50 years for drilling underground formations to recover oil and gas. Oil based fluids are preferred systems compared with water-based formulations, especially where highly water-sensitive underground formations are being drilled. In water-based fluids water tends to migrate from the fluid to the formation being drilled. This destabilizes the formation and can lead to disintegration and breakdown of the bore-hole. Furthermore, water-based fluids tend to be unsuitable for use at high temperatures and where highly deviated bore-holes may be required to reach the targeted formations.

In view of the disadvantages of water-based fluids the recent trend has been to use drilling fluids which are oil-based. However, oil-based fluids previously used containing base oils such as diesel and crude oil, are toxic and only slightly biodegradable. This is obviously unsatisfactory with respect to environmental health and safety considerations, especially as drill cuttings coated with or containing the fluid are usually discharged to the sea floor when drilling off-shore. The use of these kinds of oil-based fluids can have a detrimental effect on marine organisms.

It has been proposed to use mineral oils as the base oil in drilling fluids instead of other petroleum derived oils. However, while less toxic than these other petroleum based drilling fluids mineral oil based fluids are not very biodegradable. Surveys on drill cuttings on the seabed of the North Sea have confirmed the persistence of mineral oils.

More recently attention has focused on the use of esters, ethers and white oils as base oils. These have improved toxicity characteristics, approaching that of water, and have reasonably good aerobic biodegradability. However, with the exception of the esters they typically exhibit poor anaerobic biodegradation. Anaerobic biodegradation is required, for example, at the sea floor. Also, these base oils tend to have high kinematic viscosities and temperature limitations. Furthermore, with the exception of the white oils they are very expensive when compared to the kinds of mineral oils described above.

The present invention seeks to provide a base oil for use in oil-based well-bore fluids, such as drilling fluids, which overcomes the disadvantages discussed above. In particular, the present invention seeks to provide a base oil which has low toxicity, good aerobic and anaerobic biodegradability and a combination of physical characteristics which are especially well suited to its use as a well-bore fluid. It is also an object of the invention to provide a base oil which is inexpensive.

Accordingly, the present invention resides in the use as base oil in a well-bore fluid of a mixture comprising at least 70% by weight of one or more normal alkanes having from 11 to 16 carbon atoms, wherein the mixture has a pour point of less than -2°C.

The mixture typically comprises 30% by weight, or less, of one or more branched or cyclic alkanes having from 11 to 16 carbon atoms.

As it is extremely important that the base oil biodegrade as quickly as possible it is preferred that the mixture comprises a very high proportion of normal (straight chain) alkanes. Branched-chain and cyclic hydrocarbons are not broken down by bacteria as rapidly as normal hydrocarbons. According to a preferred embodiment of the invention the mixture comprises at least 90% by weight of the one or more normal alkanes. More preferably the mixture comprises at least about 98% by weight of the one or more normal alkanes. Mixtures of normal alkanes having from 11 to 16 carbon atoms are most preferably used.

The toxicity to flora and fauna of base oils used in drilling fluids is believed to be directly linked to aromatic content. To minimise toxicity therefore the aromatic

content in the mixture must be kept as low as possible, 0.1% by weight being the typical maximum allowed.

The pour point of drilling fluids is a particularly important characteristic as it is essential that the fluid is capable of being pumped at the lowest temperature encountered during mixing, storage, transportation and use. The pour point of the fluid is primarily influenced by the pour point of the base oil which is used.

In PCT patent application WO 95/06694, published on March 9, 1995, there is an indication on its page 4, lines 12-16, that when using normal alkanes as a drilling fluid in a cold environment, one may use a pour point depressant to reduce the pour point (freezing point) of the fluid.

In accordance with the present invention the base oil mixture has a pour point of less than -2°C, preferably -9°C or less. However, these represent the pour point of the mixture without the addition of pour point depressants. Pour point depressants could be used but they tend to be of little effect in pure normal alkane mixtures. The addition of pour point depressants may in fact lead to undesirable side-effects such as increased toxicity and low flash point. Pour point depressants may also cause decreased stability of invert emulsion well-bore fluids.

To minimise or prevent the danger of fire or explosion of oil-based drilling fluids the base oil used should have a flash point which is higher than the surface circulating temperature of the fluid during drilling of the well-bore. Preferably, the base oil used in the present invention has a flash point of at least 65°C, more preferably at least 80°C.

A further important characteristic of the base oil used is its kinematic viscosity. This is crucial to the ability of the drilling fluid to tolerate solids and water, whether added as integral components or accumulated during the mechanism of drilling into formations or by formation water intrusion. Generally, the lower the kinematic viscosity of the base oil used the higher the tolerance of the fluid is. Through practical experience it has been found that the base oil should preferably have a kinematic viscosity of from 1 to 10 cSt, more preferably from 1 to 6 cSt, at 40°C, and this is a feature of the base oil of the present invention. Base oils having a viscosity of about 1 cSt at 40°C are believed to be the most tolerant to solids and

water. Difficulty in pumping tends to be encountered when using base oils having a viscosity at 40°C of greater than 6 cSt.

Base oils which may be used in the present invention are commercially available, and tend to be produced through cracking, reaction and distillation processes.

The present invention also provides a well-bore fluid comprising as base oil the mixture as described above in combination with an emulsifier, oil-wetting agent, viscosifier, filtration control additive, rheology modifier, thinner and/or weighting agent. These are additives conventionally used in well-bore fluids and the combination which is used depends upon the desired characteristics of the fluid being formulated.

Emulsifiers which may be used include fatty acids, soaps of fatty acids and fatty acid derivatives and amidoamines, polyamides, polyamines, esters such as sorbitan monoleate polyethoxylate and sorbitan dioleate polyethoxylate, imidaxolines and alcohols.

Typical oil wetting agents which may be used include lecithin, fatty acids, crude tall oil, oxidized crude tall oil, organic phosphate esters, imidazolines, amidoamines, alkyl aromatic sulphates, alkyl aromatic sulphonates, and organic esters of polyhydric alcohols.

Typical viscosifiers include organophilic clays (eg. hectorite, bentonite and attapulgite), oil soluble polymers and resins, and polymers such as sulphonated ethylene propylene diene (EPDM) terpolymers and sulphonated butadiene styrene copolymers.

As filtration control additives which may be used there may be mentioned asphalt and derivatives thereof, gilsonite, amine-treated lignite and polymers such as EPDM terpolymers, styrene butadiene copolymers and acrylate styrene copolymers.

Typical rheology modifiers include fatty acids and polymeric fatty acids.

Thinners which may be used include petroleum sulphonates, amidoamines, alkaryl sulphonates and polyamines.

Examples of weighting agents include barite, iron oxide, iron carbonate, calcium carbonate and galena.

It is possible to use the base oils alone, i.e. without the use of the conventional additives described. Typically, however additives are required to tailor the properties of the fluid to meet specific requirements.

The well-bore fluid may be an all oil-based fluid or an invert emulsion (i.e. a water-in-oil emulsion) formed using water, brine or a polar organic liquid which is insoluble in the base oil. Preferably, the polar organic liquid is glycerol, methanol or propylene carbonate. When the well-bore fluid is an invert emulsion, the emulsified phase typically represents from 1 to 70% by volume of the fluid.

The use of fluid which is an invert emulsion enables the overall cost to be reduced by reducing the volume of base oil needed. The water activity of the invert emulsion can be adjusted by the addition of inorganic salts to balance the water activity of the formulation being drilled into. Examples of inorganic salts which may be used include the sodium, potassium, calcium, magnesium, caesium and zinc chlorides, sodium, calcium and zinc bromides, sodium, potassium and caesium formates, sodium and potassium acetates and calcium and ammonium nitrates.

The typical proportions of these additives in the well-bore fluids of the present invention are shown in the following table.

	Typical	More Typical
Base oil, Volume %	20-100	50-90
Emulsifier, lb/bbl	1-20	4-16
Oil wetting agent, lb/bbl	0-10	0.5-4
Viscosifier, lb/bbl	0-15	1-6
Filtration control additive, lb/bbl	0.5-25	1-10
Rheology modifier, lb/bbl	0-4	0.5-2
Thinner, lb/bbl	0-10	0.5-4
Weighting agent, lb/bbl	0-700	0-500
Water, Volume %	0-60	20-50
Calcium Chloride, lb/bbl (to adjust water activity)	0-150	2-100

In this table lb/bbl represents pounds per US barrel. The well-bore fluids of the present invention are prepared by conventional techniques by mixing of the

constituents. Preparation of the oil-based drilling fluid may take place at a land-based mud-mixing facility, or at the well-site. Mixing typically takes place in tanks equipped with circulating centrifugal pumps and agitation/shear equipment.

Although primarily described as a drilling fluid, the base oil described is suitable for use generally as a well-bore fluid. The base oil can be used for example as a pay zone drill in fluid, a completion fluid, a "kill" fluid, a packer fluid or casing pack, a "spotting" fluid or a "spacer".

The invention further provides a method of drilling using a well-bore fluid of the invention as described above.

The following Examples illustrate the present invention. Unless otherwise states US gallons and barrels are referred to herein.

Example 1

A laboratory barrel (350ml) of drilling fluid was prepared by mixing the various ingredients shown in the table below using a Silverson mixer at a speed of 6,000 rpm using a square hole disintegrator head. The total mixing time was 1 hour and the ingredients were added in the order listed, a period of five minutes being allowed between each ingredient addition. A water bath was used to maintain the temperature below 65°C (150°F).

TABLE 1

Ingredient	Amount	Function
Base oil A	136 ml	Base oil
EZ MUL 2F[1]	10 g	Emulsifier
GELTONE II[1]	2.5 g	Viscosifier
Lime	4 g	Alkalinity Control
DURATONE HT[1]	4 g	Filtration Control
Freshwater	136 ml	Emulsified Phase
Barite	163 g	Weighting Agent
Calcium Chloride (82% pure)	60 g	Water Activity Balance
RM-63[1]	1 g	Rheology Modifier

[1] - available from Baroid Limited

The fluid formed has the following properties:

Density	:	1.38kg/m^3 (11.5lb/gal)
Oil/Water Ratio	:	50/50
Water Phase Salinity	:	250,000 ppm calcium chloride

Base oil A has the following composition and properties:

	wt %
n-C_{11}	9.1
n-C_{12}	21.7
n-C_{13}	36.2
n-C_{14}	31.3
n-C_{15}	1.4
n-C_{16}	0.04
>C_{16}	trace
aromatics	<0.1

Pour point	= -9°C
Flash point	= 91°C
Kinematic Viscosity at 40°C	= 1.75cSt

The properties of base oil A compared with some commercially available North Sea base oils is illustrated in Table 2 below.

TABLE 2

Base Oil	Density g/ml @ 15°C	Flash Point °C (PMCC)	Aromatics % (Max)	Aniline Point °C	Kin. Viscosity cst at 40°C	Pour Point °C
Test Procedure	ASTM D129	ASTM D93	ASTM D2887	ASTM D611	ASTM D445	ASTM D97
Base Oil A	0.759	91	0.1	93	1.75	-9
BP 83 HF	0.790	95	4.5	88	2.40	-10
Fina DMF 120	0.820	74	2.3	73	1.72	nd
Fina DMF HF	0.820	103	3.9	82	2.90	-18
Total DF1	0.800	77	0.5	77	1.73	-39
Total HDF	0.814	100	6.0	86	3.20	-30
Shellsol D90	0.805	95	0.1	78	2.00	-20
Shellsol D70	0.792	72	0.5	78	1.62	-30
Clairsol 350	0.798	78	4.1	76	1.89	-35
Clairsol 450	0.815	93	4.4	88	3.40	-20
Clairsol 350MHF	0.783	94	2.0	78	2.20	-20
PETROFREE	0.860	179	0.0	na	6.00	-30

nd - not determined
na - not applicable

It can be seen from this table that base oil A compares very favourably with the other oils which are used to formulate well-bore fluids with respect to the combination of characteristics it possesses.

Example 2

The properties of a laboratory barrel (350ml) of the fluid of Example 1 were measured in accordance with API RP 13B-2. The properties of the fluid were also measured when contaminated with 35g Hymod clay, 10% by volume seawater and 10% by volume carnalite brine. The results are shown in Table 3 below.

TABLE 3

MEASURED PROPERTIES		Fluid of invention		Fluid + Hymod Clay	Fluid + Seawater	Fluid + Carnalite Brine
Hot Rolled (250°F)	hours	-	16	16	16	16
Fann 35 Readings at 120°F:						
600	rpm	85	101	159	118	96
300	rpm	55	61	104	72	59
200	rpm	43	45	85	54	45
100	rpm	33	30	61	35	30
6	rpm	16	13	26	14	11
3	rpm	14	12	24	13	10
Plastic Viscosity,	cp	28	40	55	46	37
Yield Point,	$lb/100ft^2$	27	21	49	26	22
10 sec Gel,	$lb/100ft^2$	14	13	30	13	9
10 min Gel,	$lb/100ft^2$	20	20	40	20	10
Electrical Stability	V	288	345	209	122	130
HPHT Filtrate, at 250°F,	ml	-	2.8	3.0	3.6	3.2

This table shows that the well-bore fluid of the invention is very stable to contaminants. It should be noted that the well-bore fluid exhibits very good, low rheological properties even though the water content of the fluid is 50% by volume. This shows how the low kinematic viscosity of the n-alkane mixture base oil contributes to the ability of the fluid to tolerate high added concentrations of water, and water as a contaminant.

Example 3

Following the same procedure as Example 1 a laboratory barrel (350ml) of well-bore fluid was prepared. The ingredients were mixed in the order listed in Table 4 below. Base oil A was the same as that used in Example 1.

TABLE 4

Ingredient	Amount	Function
Base Oil A	147 ml	Base oil
EZ MUL 2F[1]	20 g	Emulsifier
DURATONE HT[1]	11 g	Filtration Control
XP-10[1] (Experimental product)	3.5 g	Filtration Control
BENTONE 38[2]	0.5 g	Viscosifier
SUSPENTONE[1]	4 g	Viscosifer
Lime	4 g	Alkalinity Control
Freshwater	28 ml	Emulsified Phase
Barite	589 g	Weighting Agent
Calcium Chloride (82% pure)	9.7 g	Water Activity Balance
RM-63[1]	0.75 g	Rheology Modifier

[1] - available from Bariod Limited
[2] - available from Rheox

The fluid formed has the following properties:

Density	: 2.24kg/m^3 (18.67 lb/gal)
Oil/Water Ratio	: 85/15
Water Phase Salinity	: 250,000 mg/L calcium chloride

EXAMPLE 4

Example 2 was repeated using a laboratory barrel of the well-bore fluid of Example 3. The contaminants used were Hymod clay (35g) and seawater (10% by volume). The fluid was hot rolled at the temperatures shown in Table 5 below. This table shows the properties of the fluid.

TABLE 5

MEASURED PROPERTIES									
		Fluid of the Invention				Fluid + Hymod Clay		Fluid + Seawater	
Hot Rolled (350°F)	hours	-	16	-	-	-	-	-	-
Hot Rolled (395°F)	hours	-	-	16	-	16	-	16	-
Static Aged (395°F)	hours	-	-	-	16	-	16	-	16
600/300	rpm	130/75	132/78	131/74	165/98	182/111	183/120	136/85	168/109
200/100	rpm	58/38	61/40	58/37	74/48	88/62	97/68	67/27	87/61
6/3	rpm	12/10	16/14	14/12	17/15	28/27	28/24	16/14	24/20
Plastic Viscosity	cp	55	54	57	67	71	63	51	59
Yield Point	$lb/100ft^2$	20	24	17	31	40	57	34	50
10 sec Gel	$lb/100ft^2$	12	16	22	18	26	28	22	23
10 min Gel	$lb/100ft^2$	21	21	24	26	32	36	25	28
Electrical Stability	V	1393	1218	1484	1002	1215	1560	713	1211
HTHP fluid loss, ml @ 395°F			5.4	5.8	11.2	8.2	14.0	6.4	12.0

The results confirm the stability of the fluids of the invention even when exposed at high temperature to contaminants.

What is claimed is:

1. A base oil for use in a well-bore fluid of a mixture comprising at least 70% by weight of one or more normal alkanes having from 11 to 16 carbon atoms, with no more than a trace of said normal alkanes having greater than 16 carbon atoms, wherein the mixture has a pour point of less than -2°C without containing a pour point depressant.

2. The base oil according to Claim 1, wherein the mixture comprises up to 0.1% by weight aromatics.

3. The base oil according to Claims 1 or 2, wherein the mixture comprises 30% by weight, or less, of one or more branched or cyclic alkanes having from 11 to 16 carbon atoms.

4. The base oil according to any one of Claims 1 to 3, wherein the mixture comprises at least 90% by weight of one or more normal alkanes.

5. The base oil according to Claim 4, wherein the mixture comprises at least about 98% by weight of one or more normal alkanes.

6. The base oil according to any one of the preceding claims, wherein the mixture has a pour point of -9°C or less.

7. The base oil according to any one of the preceding claims, wherein the mixture has a flash point of at least 65°C.

8. The base oil according to Claim 7, wherein the mixture has a flash point of at least 80°C.

9. The base oil according to any of the preceding claims, wherein the mixture has a kinematic viscosity at 40°C of from 1 to 10 cSt.

10. The base oil according to Claim 9, wherein the mixture has a kinematic viscosity at 40°C of from 1 to 6 cSt.

11. A well-bore fluid comprising as base oil a mixture as defined in any one of Claims 1 to 10 in combination with one or more of an emulsifier, oil-wetting agent, viscosifier, filtration control additive, rheology modifier thinner, weighting agent and/or other well-bore fluid additive.

12. A fluid according to Claim 11 comprising from 20% to 100% by weight of base oil mixture, based on the total weight of the fluid.

13. A fluid according to Claims 11 or 12 which is an all oil-based fluid.

14. A fluid according to Claims 11 or 12 which is an invert emulsion with water, brine or a polar organic liquid which is insoluble in the base oil mixture.

15. A fluid according to Claim 14, wherein the polar organic liquid is glycerol, methanol or propylene carbonate.

16. A method of drilling a well which comprises using as drilling fluid the drilling fluid defined in any one of Claims 11 to 15.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/00993

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :Please See Extra Sheet.
US CL : 585/1,2; 507/100,103,110,111,116,117,118,119
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 585/1,2; 507/100,103,110,111,116,117,118,119

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO,A, 8302949; (Jachnik); 01 September 1983; see page 7, lines 3-4 and 21-34 and page 10, lines 4-10.	1-3
X --,P Y	WO, A 95 006694 (Sawdon); 09 March 1995; see page 2, lines 21-25, column 6, lines 5-18.	1-3 --- 1-3
Y	US,A 4,508,628 (Walker et al); 02 April 1985; see column 4, lines 45-59.	1-3
Y	US,A, 5,333,698 (Van Slyke); 02 August 1994; see column 2, lines 10-24.	1-3

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
18 APRIL 1996	14 MAY 1996
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer ELIZABETH D. IRZINSKI Telephone No. (703) 308-3802

Form PCT/ISA/210 (second sheet)(July 1992)*

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/00993

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 4-16
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.

Form PCT/ISA/210 (continuation of first sheet(1))(July 1992)*

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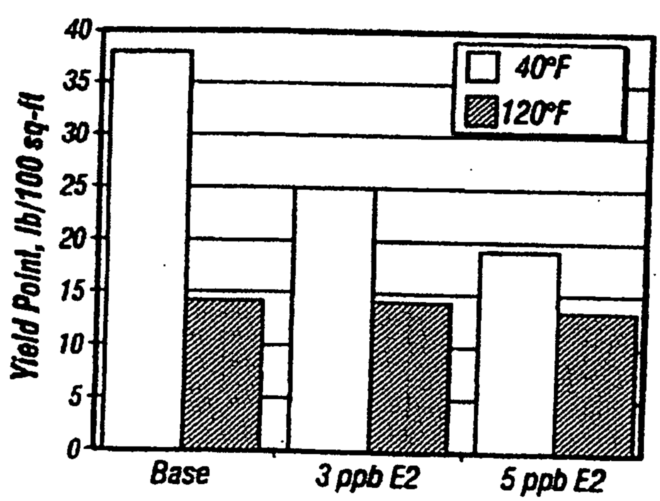
For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: THINNERS FOR INVERT EMULSIONS



(57) Abstract: A method of reducing the viscosity of oil-based drilling fluids and well service fluids at low temperatures and a thinner compound for use in such drilling fluids and well service fluids is disclosed. The method comprises adding to said drilling fluids or well service fluids a thinner having the formula: $R\text{-}(C_2H_4O)_n(C_3H_6O)_m(C_4H_8O)_k\text{-}H$ where R is a saturated or unsaturated, linear or branched alkyl radical having about 8 to about 24 carbon atoms, n is a number ranging from about 1 to about 10, m is a number ranging from about 0 to about 10, and k is a number ranging from about 0 to about 10.

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International Application No.

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REQUEST

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty.

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THINNERS FOR INVERT EMULSIONS

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THINNERS FOR INVERT EMULSIONS

Background of the Invention

1. Field of the Invention

This invention is generally related to methods and compositions for drilling and servicing wellbores in hydrocarbon bearing subterranean formations. Particularly, this invention is related to oil-based drilling fluid systems comprising water-in-oil invert emulsions, and to thinners that enhance or enable use of such fluids, at temperatures at or below about 50 degrees Fahrenheit (about 10 degrees Centigrade).

2. Description of Relevant Art

A drilling fluid, or "mud" which a drilling fluid is also often called, is a specially designed fluid that is circulated in a wellbore as the wellbore is being drilled to facilitate the drilling operation. The various functions of a drilling fluid include removing drill cuttings from the wellbore, cooling and lubricating the drill bit, aiding in support of the drill pipe and drill bit, and providing a hydrostatic head to maintain the integrity of the wellbore walls and prevent well blowouts. Specific drilling fluid systems are selected to optimize a drilling operation in accordance with the characteristics of a particular geological formation.

A drilling fluid typically comprises water and/or oil or synthetic oil or other synthetic material or synthetic fluid ("synthetic") as a base fluid, with solids in suspension. A non-aqueous based drilling fluid typically contains oil or synthetic as a continuous phase and may also contain water dispersed in the continuous phase by emulsification so that there is no distinct layer of water in the fluid. Such dispersed water in oil is generally referred to as an invert emulsion or water-in-oil emulsion.

A number of additives may be included in such oil based drilling fluids and invert emulsions to enhance certain properties of the fluid. Such additives may include, for example, emulsifiers, weighting agents, fluid-loss additives or fluid-loss control agents, viscosifiers or viscosity control agents, and alkali. Further general discussion and description of oil-based drilling fluids is provided in P.A. Boyd, et al., New Base Oil Used In Low Toxicity Oil Muds, Journal of

Petroleum Technology, pages 137-142 (1985), which is incorporated herein by reference.

An essential criterion for assessing the utility of a fluid as a drilling fluid or as a well service fluid is the fluid's rheological parameters, particularly under drilling and wellbore conditions. For use as a drilling fluid, or as a fluid for servicing a well, the fluid must be capable of maintaining certain viscosities suitable for drilling and circulation in the wellbore. Preferably, a drilling fluid will be sufficiently viscous to be capable of supporting and carrying to the surface of the well drill cuttings without being so viscous as to interfere with the drilling operation. Moreover, a drilling fluid must be sufficiently viscous to be able to suspend barite and other weighting agents. However, increased viscosity can result in problematic sticking of the drill string, and increased circulating pressures can contribute to lost circulation problems.

Thinners may be added to the drilling fluid or drilling mud systems before and in the course of drilling. Anionic surfactants particularly from the group of the fatty alcohol sulfates, the fatty alcohol ether sulfates and the alkylbenzenesulfonates are examples of such thinners known in the prior art. Although such compounds have been shown to effect thinning of drilling fluids, problems with such prior art thinners may occur when using the drilling muds at low temperatures (temperatures at or below about 50°F (10° C)).

At such low temperatures, despite the use of known prior art thinners, oil based drilling fluids typically have high or increased viscosity, which may render the fluids unusable for drilling. After pumping into the wellbore, drilling fluids may undergo heating from the formation, depending on the depth of the wellbore and the temperature of the formation. For example, heating in the range of about 150° to about 250°F (about 66° to about 121°C) is not uncommon and subterranean temperatures as high as about 350°F (about 178°C), particularly in very deep wellbores, are known. The Arctic region, for example, is known to have very low surface temperatures but very high subterranean temperatures. Even more problematic are deepwater wells (i.e., typically wells below at least about 1500 feet), which subject drilling fluids to chilling from cold waters surrounding the riser as the fluid returns to the surface from the high temperature subterranean formation. Such chilling of oil

based drilling fluids typically increases their viscosity while such subterranean heating of oil based drilling fluids typically reduces their viscosity.

Preferably, thinners which reduce the viscosity of drilling fluids at low temperatures will not affect the viscosity of the fluids at high temperatures. That is, in many cases, a thinner is desired that is capable of "selectively" influencing the rheology or particularly reducing the viscosity of oil-based drilling fluids only at lower temperatures, such as may be encountered at the ground surface of the wellbore, or in the riser surrounded by waters above a deepwater offshore well, for example.

Thinners and other additives to drilling fluids, as well as drilling fluids employed in onshore and offshore wells, must commonly meet stringent environmental regulations related to biodegradability and toxicity. Further, drilling fluids and additives to drilling fluids must be able to withstand subterranean conditions that the fluids will typically encounter in a wellbore, such as high temperatures, high pressures, and pH changes.

A need exists for improved rheology-modifying or viscosity reducing additives to oil-based drilling fluids, and particularly to drilling fluids comprising invert (water-in-oil) emulsions, which are expected to be used in or to encounter low temperatures in drilling operations. As used herein, unless indicated otherwise, "low temperatures" shall be understood to mean temperatures at or below about 50°F (about 10°C).

Summary of the Invention

According to the method of the present invention, a compound is added to a water-in-oil or invert emulsion drilling fluid or well service fluid which reduces the viscosity of the drilling fluid or well service fluid at low temperatures or which enables or enhances the ability of the drilling fluid or well service fluid to maintain its viscosity at low temperatures. The compound, which may be generally called a "thinner," continues to have this effect on a drilling fluid or well service fluid in drilling or servicing wellbores in subterranean formations, particularly hydrocarbon bearing subterranean formations. Further, this compound does not significantly affect the viscosity of the emulsion at high temperatures.

The compound has the following formula:

$$R\text{-}(C_2H_4O)_n(C_3H_6O)_m(C_4H_8O)_k\text{-}H$$

where R is a saturated or unsaturated, linear or branched alkyl radical having about 8 to about 24 carbon atoms, n is a number ranging from about 1 to about 10, m is a number ranging from about 0 to about 10, and k is a number ranging from about 0 to about 10.

The invention also comprises the composition of a water-in-oil or invert emulsion drilling fluid or well service fluid containing this thinner compound.

Brief Description of the Drawings

Figure 1 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 2 at different temperatures.

Figure 2 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 3 at different temperatures.

Figure 3 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 4 at different temperatures.

Figure 4 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 5 at different temperatures.

Figure 5 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 6 at different temperatures.

Figure 6 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 7 at different temperatures.

Figure 7 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 8 at different temperatures.

Figure 8 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 9 at different temperatures.

Detailed Description of Preferred Embodiments

The present invention provides a method of influencing the rheology, and particularly reducing the viscosity, of drilling fluids or well service fluids comprising invert (water-in-oil) emulsions. The method is particularly applicable to fluids for use in wellbores penetrating hydrocarbon bearing subterranean formations and has particular advantage in applications where the fluids are subjected to low temperatures, as in drilling or in servicing deepwater offshore wells. Such drilling fluids and well service fluids typically comprise a continuous oil phase, water dispersed in the oil phase, solids insoluble in the drilling fluid or well service fluid suspended in the fluid, and various additives. As the term is used herein, "invert emulsion" or "oil-in-water emulsion" is understood to mean the liquid portion of the drilling fluid comprising an emulsion (excluding solids). The term "invert emulsion drilling fluid" means the total sum of what is circulated as a drilling fluid.

In the method of this invention, a composition or compound having the following formula (I) is added to the invert emulsion or oil-based drilling fluid (or well service fluid) to reduce the viscosity of the fluid or to enhance the ability of the fluid to maintain its viscosity or to resist increasing viscosity at low temperatures. The compound may be added to the fluid during initial preparation of the fluid or later as the fluid is being used for drilling or well service purposes in the formation. The quantity added is an effective amount to maintain or effect the desired viscosity of the drilling fluid. For purposes of this invention, an "effective amount" of thinner of formula (I) is preferably from about 0.5 to about 15 pounds per barrel of drilling fluid or mud. A more preferred amount of thinner ranges from about 1 to about 5 pounds per barrel of drilling fluid and a most preferred amount is about 1.5 to about 3 pounds thinner per barrel of drilling fluid.

Formula (I) is:

(I) $R\text{-}(C_2H_4O)_n(C_3H_6O)_m(C_4H_8O)_k\text{-}H$

where R is a saturated or unsaturated, linear or branched, alkyl radical having about 8 to about 24 carbon atoms, n is a number ranging from about 1 to about 10, m is a number ranging from about 0 to about 10, and k is a number ranging from about 0 to about 10. Preferably, R has about 8 to about 18 carbon atoms; more preferably, R has about 12 to about 18 carbon atoms; and most preferably, R has about 12 to about 14 carbon atoms. Also, most preferably, R is saturated and linear.

The compositions or compounds of formula (I) may be prepared by customary techniques of alkoxylation, such as alkoxylating the corresponding fatty alcohols with ethylene oxide and/or propylene oxide or butylene oxide under pressure and in the presence of acidic or alkaline catalysts as is known in the art. Such alkoxylation may take place blockwise, i.e., the fatty alcohol may be reacted first with ethylene oxide, propylene oxide or butylene oxide and subsequently, if desired, with one or more of the other alkylene oxides. Alternatively, such alkoxylation may be conducted randomly, in which any desired mixture of ethylene oxide, propylene oxide and/or butylene oxide is reacted with the fatty alcohol.

In formula (I), the subscripts n and m respectively represent the number of ethylene oxide (EO) and propylene oxide (PO) molecules or groups in one molecule of the alkoxylated fatty alcohol. The subscript k indicates the number of butylene oxide (BO) molecules or groups. The subscripts n, m, and k need not be integers, since they indicate in each case statistical averages of the alkoxylation. Included without limitation are those compounds of the formula (I) whose ethoxy, propoxy, and/or butoxy group distribution is very narrow, such as for example, "narrow range ethoxylates" also called "NREs" by those skilled in the art.

To accomplish the purposes of this invention, the compound of formula (I) must contain at least one ethoxy group. Preferably, the compound of formula I will also contain at least one propoxy group (C_3H_6O-) or butoxy group (C_4H_8O-). Mixed alkoxides containing all three alkoxide groups—ethylene oxide, propylene oxide, and butylene oxide—are possible for the invention but are not preferred.

Preferably, for use according to this invention, the compound of formula (I) will have a value for m ranging from about 1 to about 10 with k zero or a value for k ranging from about 1 to about 10 with m zero. Most preferably, m will be about 1 to about 10 and k will be zero.

Other preferred compounds for use in the invention having the formula (I) above will have n ranging from about 1 to about 6, m ranging from about 1 to about 6, and k zero. Still other preferred compounds for use in the invention having the formula (I) above will have n ranging from about 2 to about 5, and m being about 3 or about 4 with k zero. It is particularly advantageous to establish the distribution of ethylene oxide and propylene oxide groups in the compounds of formula (I) in an ethylene oxide to propylene oxide ratio of about 1:1 to about 2:1, or even more preferably, about 2:1.5.

Additional preferred compounds for use in the invention having formula (I) above will have alkyl radicals containing about 12 to about 18 carbon atoms, or more preferably about 12 to about 14 carbon atoms, with subscripts n and m each having values of about 4 or about 5.

Used as thinners according to the method of the invention, the compounds of formula (I) reduce the viscosity or lower the yield point of the drilling fluid to which they are added. These thinners are particularly effective at low temperatures, i.e., temperatures at or below about 50°F (about 10°C) and most particularly effective at temperatures at or below about 40°F (about 4°C). The lower limit of effectiveness for these thinners is about 14°F (about –10°C). The thinners do not significantly influence or affect the rheology of drilling fluids at high temperatures, particularly temperatures ranging from about 100 to about 250° F or more.

The compounds of formula (I) are biodegradable and are of little or no toxicity. They are expected to be capable of meeting increasingly stringent environmental regulations affecting the oil and gas industry worldwide.

Example drilling fluids comprising invert (water-in-oil) emulsions of particular use in the method of the invention generally have an oil phase comprising diesel oil, paraffin oil and/or mineral oil, or a synthetic oil. Alternatively, other carrier fluids may be used such as carboxylic esters, alcohols, ethers, internal olefins, alphaolefins (IO and/or AO), and

polyalphaolefins (PAO), which may be branched or unbranched but are preferably linear and preferably ecologically acceptable (non-polluting oils). Preferably, the oils or carrier fluids used for the oil phase of the drilling fluid will be comprised of compounds which are flowable and pumpable at temperatures above about 32°F (about 0°C) or at least as low as about 40°F (about 5°C) as well as at higher temperatures. For example, compounds selected from one or more of the following groups or classes below are believed particularly suitable to comprise the oil phase of drilling fluids used in the present invention:

(a) most preferably, carboxylic esters of the formula:

$$R'\text{-}COO\text{-}R'' \qquad (II)$$

where R' is a saturated or unsaturated, linear or branched, alkyl radical having about 5 to about 23 carbon atoms and R" is an alkyl radical, branched or unbranched, saturated or unsaturated, having about 1 to about 22 carbon atoms;

(b) also preferably, linear or branched olefins having about 8 to about 30 carbon atoms;

(c) water-insoluble symmetric or asymmetric ethers of monohydric alcohols of natural or synthetic origin, said alcohols containing about 1 to about 24 carbon atoms;

(d) water-insoluble alcohols of the formula:

$$R'''\text{-}OH \qquad (III)$$

where R'" is a saturated, unsaturated, linear or branched alkyl radical having about 8 to about 24 carbon atoms; and

(e) carbonic diesters.

Such suitable oils are taught further, for example, in: European Patent Applications 0 374 671, 0 374,672, 0 382 070, and 0 386 638 of Cognis; European Laid-Open Specification 0 765 368 of Cognis (linear olefins); European Application 0 472 557 (water insoluble symmetric or asymmetric ethers of monohydric alcohols of natural or synthetic origin containing about 1 to about 24 carbon atoms); European Application 0 532 570 (carbonic

diesters). Carboxylic esters of formula (II) above are preferred for the oil phase of drilling fluids used in this invention and particularly preferred are the esters described in European Laid-Open Specification EP 0 374 672 and EP 0 386 636.

In a preferred embodiment of this invention, compounds of formula (I) are added to drilling fluids comprising invert emulsions having an oil phase comprising esters of formula (II) where the radical R' in formula (II) is an alkyl radical having about 5 to about 21 carbon atoms (or more preferably about 5 to about 17 carbon atoms or most preferably about 11 to about 17 carbon atoms). Particularly suitable alcohols for making such esters are branched or unbranched alcohols with about 1 to about 8 carbon atoms, for example, methanol, isopropanol, isobutanol, and 2-ethylhexanol. Alcohols having about 12 to about 18 carbon atoms may alternatively be preferred for making other esters suitable for the invention.

For example, additional preferred esters for the oil phase of drilling fluids used in the invention include, without limitation: saturated C12-C14 fatty acid esters and unsaturated C16-C18 fatty acids (with isopropyl-, isobutyl- or 2-ethylhexanol as the alcohol component); 2-ethylhexyl octanoate; acetic acid esters, especially acetates of C8-C18 fatty alcohols; branched carboxylic esters disclosed in WO 99/33932 of Chevron or EP 0 642 561 of Exxon; alpha olefin mixtures disclosed in EP 0 765 368 A1 of Cognis and Halliburton; and blends of these various esters.

The oil phase of the emulsions of the drilling fluids used in the invention is preferably comprised of at least about 50 % by volume of one or more preferred compounds (a) – (e) above. More preferably, such preferred compounds comprise about 60% to about 80% by volume of said oil phase, and most preferably, such preferred compounds comprise about 100% of the oil phase.

Water is preferably present in the liquid phase of the drilling fluids used in the invention, and preferably in amounts not less than about 0.5% by volume (excluding solids in the liquid phase). In a preferred embodiment of this invention, thinners of formula (I) are added to drilling fluids comprising invert emulsions containing about 15 to about 35% by volume water and more

preferably 20% by volume water and about 80% by volume oil phase. To compensate for the osmotic gradient between the drilling mud and the formation or connate water, water in drilling fluids used in the present invention typically includes fractions of electrolytes, such as calcium salts and/or sodium salts. $CaCl_2$ in particular is frequently used, although other salts from the group of alkali metals and/or alkaline earth metals are also suitable, with potassium acetates and formates being common examples.

Preferred drilling fluids used in this invention have the following rheology: plastic viscosity (PV) in the range of about 10 to about 60 cP, and preferably in the range of about 15 to about 40 cP, and yield point (YP) in the range of about 5 to about 40 lb/100 ft^2, and preferably in the range of about 10 to about 25 lb/100 ft^2, at about 122°F (about 50°C). At lower temperatures, i.e., at or below about 40°F (about 4°C), the YP should not exceed about 75 lb/100 ft^2, and should preferably be in the range of about 10 to about 65 lb/100 ft^2, more preferably about 15 to about 45 lb/100 ft^2, and most preferably less than about 35 lb/100 ft^2. A preferred practicable lower limit for YP for drilling fluids used in this invention is about 5 lb/100 ft^2.

Methods for determining these parameters of PV and YP are well known to those skilled in the art. An example reference is "Manual of Drilling Fluids Technology", particularly the chapter on Mud Testing, available from Baroid Drilling Fluids, Inc., in Houston, Texas (USA), incorporated herein by reference.

The solids content (not including low gravity solids), or the amount of weighting agents, in drilling fluids used in this invention is preferably about 0 to about 500 lb/bbl, and most preferably about 150 to about 350 lb/bbl. The mud weight, i.e., the density of the drilling fluids, is preferably in the range of about 8 to about 18 lb/gal. and more preferably about 9 to about 15 lb/gal. Such solids, or weighting agents, which serve to increase the density of the drilling fluids, may be any solids known to those skilled in the art as useful for such purpose, but will preferably be inert or environmentally friendly.

Drilling fluids used in this invention may optionally also contain other additives known to those skilled in the art, such as fluid-loss control additives and emulsifiers. Alkali may also be used, preferably lime (calcium hydroxide

or calcium oxide), to bind or react with acidic gases (such as CO_2 and H_2S) encountered during drilling in the formation. Such alkali, or an alkali reserve, is known to prevent hydrolysis by acidic gases of generally acid-labile esters of the drilling fluid. Preferred quantities of free lime in the drilling fluids range from about 1 to about 10 lbs/bbl, and more preferably about 1 to about 4 lbs/bbl, although lower ranges such as less than about 2 lbs/bbl are preferred for certain esters that tend to hydrolyze in the presence of alkaline compounds as will be known to those skilled in the art. Other suitable agents as an alternative to lime may also be used to adjust and/or stabilize invert emulsions of the drilling fluids with respect to acids. An example of such alternative agents is a protonated amine, as described in U.S Patent No. 5,977,031.

Further optional additives that may be present in the drilling fluids used in this invention include electrolytes, such as calcium chloride, organophilic bentonite and organophilic lignite. Glycols and/or glycerol may also be added. Still further, dispersion aids, corrosion inhibitors and/or defoamers may be used. These and other suitable auxiliaries and additives are used in amounts known to those skilled in the art depending on the conditions of the particular wellbore and subterranean formation.

Although the invention has primarily been described in the context of a method of using compounds of formula (I) as thinners for drilling fluids at low temperatures, the compounds of formula (I) may also be effective as thinners for well service fluids such as spotting fluids or workover fluids at low temperatures.

Further description and use of the invention is shown by the following examples:

Examples

To show the effect of the invention, the following experiments were conducted. In each case an invert emulsion drilling mud system of the following general composition was prepared:

Ester	bbl	0.496
Water	bbl	0.233
Emulsifier	lb	6.0
Organophilic bentonite	lb	1.0
Organophilic lignite	lb	5.0
Alkali reserve (lime)	lb	1.5
$CaCl_2 \times 2\ H_2O$	lb	27.2
Barite	lb	314.0
Dispersing auxiliary	lb	0.5
Thinner	lb/bbl	2.0

The oil phase (A) used was a 2-ethylhexyl octanoate as disclosed in EP 0 386 636. The emulsifier used was the product EZ MUL NTE (Baroid Drilling Fluids Inc., Houston, Texas). The oil/water ratio was 70/30 in each case. Measurements were carried out on a system without thinner (C1), and with a $C_{12/14}$ fatty alcohol sulfate + 2 EO, sodium salt (C2), with a C_{12} ether sulfate, sodium salt (C3) and with an oleic acid sulfonate disodium salt (C4), respectively, as prior art thinners, and comparison was made with these thinners and with compounds of formula (I) in accordance with the invention. The formula (I) compounds used for this purpose were as follows:

E1 C12/C14 fatty alcohol containing 2 EO and 4 PO
E2 C12/C14 fatty alcohol containing 5 EO and 4 PO
E3 C12/C18 fatty alcohol containing 5 EO and 4 PO
E4 C12/C14 fatty alcohol containing 6 EO and 4 PO

The invert muds were prepared in a conventional manner and subsequently, at 40°F and 122°F, the rheological characteristics of plastic viscosity (PV) and yield point (YP) and the gel strength after 10 seconds and 10 minutes using a Fann SR12 rheometer (from Fann) were determined.

Measurements E5, E6 and E7 were carried out using the thinners E1, E2 and E4, but in contrast to the details above, 45 lb of solids (rev dust, i.e., filter ash) were also added to each of the muds, in order to demonstrate the advantageous action of the compounds of formula (I) used in accordance with the invention in the case of high solids loading of the emulsions. In these cases, the measurements were taken only after 16 hours of aging at 150°F. The thinner was not added to the muds E5 to E7 until after aging.

The results of the measurements are given in Tables 1a and 1b below:

Table 1a

	C1	C1	C2	C2	C3	C3	C4	C4	E1	E1	E2	E2	E3	E3	E4	E4
Temp. °F	40	122	40	122	40	122	40	122	40	122	40	122	40	122	40	122
PV (cP)	94	28	105	30	n.m.	33	91	24	93	31	87	28	94	28	83	29
YP lb/100 ft^2	68	29	71	35	n.m.	62	69	20	70	41	34	33	62	41	30	30
Gels 10"/10'	27/29	12/13	24/29	15/15	n.m.	26/31	25/25	6/7	25/28	17/19	11/13	14/16	20/24	17/18	8/11	13/14

n.m : not measurable

Table 1b - Measurements with addition of 45 lb rev dust

	C1	C1	E5	E5	E6	E6	E7	E7
Temperature °F	40	122	40	122	40	122	40	122
PV (cP)	94	28	107	37	108	40	106	37
YP lb/100 ft^2	68	29	37	23	72	42	46	30
Gels 10"/10'	27/29	12/13	12/14	7/9	26/30	14/18	17/19	12/14

The data, especially for the yield point (YP), clearly indicate the advantageous thinning effect of the compounds of formula (I) used in the method and in the emulsions of the invention, especially at low temperatures, in comparison to the prior art. The higher plastic viscosity for E5 to E7 is attributable to the higher proportion of solids in the mud systems.

Further experiments may be seen in Tables 2 to 9. In these cases, the yield point (YP) of the systems tested was investigated at different temperatures and depicted as a graph. This illustrates particularly well the advantageous influence of the compounds of formula (I) on the rheology at low temperatures (40°F, 4°C) without any marked influence at high temperatures (120°F, 50°C). The measurements were carried out using a Fann 35 viscometer (from Fann). The tables also indicate the dial readings at different speeds of rotation per minute (rpm).

In Tables 2 to 9:

PETROFREE LV ®	is 2-ethylhexyl octanoate (from Cognis, Germany)
PETROFREE LE®	is linear alpha-olefin (from Cognis, Germany)
PETROFREE®	is C8-14 fatty acid 2-ethylhexyl ester (from Cognis, Germany)
GELTONE II®	is organophilic bentonite (from Baroid, Houston, Texas)
Thinner E1	is Formula I C12/C14 fatty alcohol of the invention containing 2 EO and 4 PO
Thinner E2	is Formula I C12/C14 fatty alcohol of the invention containing 5 EO and 4PO

Table 2

Mud system	PETROFREE LV					
Mud weight, lb/gal	14.0					
Oil/water ratio	70/30					
Contaminant	Drill solids					
E2, lb/bbl	0		3		5	
Temperature, °F	40	120	40	120	40	120
Plastic viscosity, cP	118	40	113	34	107	35
Yield point, $lb/100ft^2$	38	14	25	14	19	13
10 sec gel, $lb/100ft^2$	16	6	10	6	6	6
10 min gel, $lb/100ft^2$	22	11	13	8	9	8
Fann 35 dial readings						
600 rpm	274	94	251	82	233	83
300 rpm	156	54	138	48	126	48
200 rpm	114	40	97	35	88	35
100 rpm	70	25	56	22	49	22
6 rpm	17	6	10	7	7	6
3 rpm	14	5	7	6	5	5

Table 3

Mud system	PETROFREE			
Mud weight, lb/gal	14.0			
Oil/water ratio	75/25			
Contaminant	Excess GELTONE II			
E2, lb/bbl	0		3	
Temperature, °F	40	120	40	120
Plastic viscosity, cP	180	51	126	50
Yield point, $lb/100ft^2$	230	152	19	125
10 sec gel, $lb/100ft^2$	108	64	10	50
10 min gel, $lb/100ft^2$	110	66	13	52
Fann 35 dial readings				
600 rpm	590	254	271	225
300 rpm	410	203	145	175
200 rpm	336	179	103	149
100 rpm	248	146	59	119
6 rpm	112	79	10	62
3 rpm	100	70	8	58

Table 4

Mud system	PETROFREE LV			
Mud weight, lb/gal	16.0			
Oil/water ratio	80/20			
Contaminant	Drill solids			
E2, lb/bbl	0		3	
Temperature, °F	40	120	40	120
Plastic viscosity, cP	152	51	142	40
Yield point, lb/100ft^2	62	27	40	19
10 sec gel, lb/100ft^2	22	10	18	10
10 min gel, lb/100ft^2	48	26	22	12
Fann 35 dial readings				
600 rpm	366	129	324	99
300 rpm	214	78	182	59
200 rpm	158	59	130	45
100 rpm	98	38	78	30
6 rpm	24	11	16	10
3 rpm	20	9	12	9

Table 5

Mud system	PETROFREE			
Mud weight, lb/gal	11.0			
Oil/water ratio	70/30			
Contaminant	Excess GELTONE II			
E2, lb/bbl	0		3	
Temperature, °F	40	120	40	120
Plastic viscosity, cP	132	31	88	29
Yield point, lb/100ft^2	54	53	37	53
10 sec gel, lb/100ft^2	33	23	13	26
10 min gel, lb/100ft^2	38	27	17	30
Fann 35 dial readings				
600 rpm	318	115	213	111
300 rpm	186	84	125	82
200 rpm	139	71	90	70
100 rpm	91	54	56	55
6 rpm	35	25	15	28
3 rpm	32	21	13	25

Table 6

Mud system	PETROFREE			
Mud weight, lb/gal	11.0			
Oil/water ratio	70/30			
Contaminant	Drill solids			
E2, lb/bbl	0		3	
Temperature, °F	40	120	40	120
Plastic viscosity, cP	110	34	113	34
Yield point, lb/100ft^2	90	47	73	44
10 sec gel, lb/100ft^2	38	21	27	20
10 min gel, lb/100ft^2	44	24	30	22
Fann 35 dial readings				
600 rpm	310	115	299	112
300 rpm	200	81	186	78
200 rpm	157	67	142	64
100 rpm	110	50	95	48
6 rpm	42	23	31	22
3 rpm	38	21	27	19

Table 7

Mud system	PETROFREE LE			
Mud weight, lb/gal	16.4			
E2, lb/bbl	0		3	
Temperature, °F	40	120	40	120
Plastic viscosity, cP	173	40	107	43
Yield point, lb/100ft^2	21	9	18	7
10 sec gel, lb/100ft^2	16	8	11	8
10 min gel, lb/100ft^2	19	11	15	11
Fann 35 dial readings				
600 rpm	367	89	232	93
300 rpm	194	49	125	50
200 rpm	135	35	88	37
100 rpm	74	22	50	22
6 rpm	12	5	9	6
3 rpm	10	4	7	5

Table 8

Mud system	PETROFREE LE			
Mud weight, lb/gal	11.6			
E2, lb/bbl	0		3	
Temperature, °F	40	120	40	120
Plastic viscosity, cP	80	31	56	32
Yield point, lb/100ft^2	25	18	27	16
10 sec gel, lb/100ft^2	12	8	17	9
10 min gel, lb/100ft^2	20	11	23	11
Fann 35 dial readings				
600 rpm	185	80	139	80
300 rpm	105	49	83	48
200 rpm	77	37	63	37
100 rpm	46	24	43	24
6 rpm	11	7	14	8
3 rpm	9	6	13	7

Table 9

Mud system	PETROFREE LV			
Mud weight, lb/gal	14.0			
Oil/water ratio	70/30			
Contaminant	Drill solids			
E1, lb/bbl	0		3	
Temperature, °F	40	120	40	120
Plastic viscosity, cP	118	40	113	35
Yield point, lb/100ft^2	38	14	41	16
10 sec gel, lb/100ft^2	16	6	16	9
10 min gel, lb/100ft^2	22	11	20	11
Fann 35 dial readings				
600 rpm	274	94	267	86
300 rpm	156	54	154	51
200 rpm	114	40	114	39
100 rpm	70	25	71	26
6 rpm	17	6	18	8
3 rpm	14	5	14	8

The foregoing description of the invention is intended to be a description of preferred embodiments. Various changes in the details of the described composition and method can be made without departing from the intended scope of this invention as defined by the appended claims.

We claim:

1. A method of influencing the rheology of a drilling fluid or well service fluid comprising an invert emulsion, said method comprising adding to said drilling fluid or well service fluid a compound having the formula:

$$R\text{-}(C_2H_4O)_n(C_3H_6O)_m(C_4H_8O)_k\text{-}H$$

where R is a saturated or unsaturated, linear or branched alkyl radical having about 8 to about 24 carbon atoms, n is a number ranging from about 1 to about 10, m is a number ranging from about 0 to about 10, and k is a number ranging from about 0 to about 10.

2. The method of claim 1 wherein in said formula, k is zero and m is a number ranging from about 1 to about 10, or m is zero and k is a number ranging from about 1 to about 10.

3. The method of claim 1 wherein in said formula, n is a number ranging from about 1 to about 6, m is a number ranging from about 1 to about 6, and k is zero.

4. The method of claim 1 wherein said invert emulsion comprises a continuous oil phase comprising compounds or compositions flowable and pumpable at temperatures at least as low as about 40 degrees Fahrenheit.

5. The method of claim 1 wherein said invert emulsion comprises a continuous oil phase comprising compounds or compositions flowable and pumpable at temperatures above about 32 degrees Fahrenheit.

6. The method of claim 5 wherein said oil phase comprises compounds or compositions selected from the group comprising:

(f) carboxylic esters of the formula:

R'-COO-R"

where R' is a saturated or unsaturated, linear or branched, alkyl radical having about 1 to about 23 carbon atoms and R" is an alkyl radical, branched or unbranched, saturated or unsaturated, having about 1 to about 23 carbon atoms;

(g) linear or branched olefins having about 8 to about 30 carbon atoms;

(h) water-insoluble symmetric or asymmetric ethers of monohydric alcohols of natural or synthetic origin, said alcohols containing about 1 to about 24 carbon atoms;

(i) water-insoluble alcohols of the formula:

R'"-OH

where R'" is a saturated, unsaturated, linear or branched alkyl radical having about 8 to about 24 carbon atoms; and

(j) carbonic diesters.

7. The method of claim 1 wherein said compound is added to said drilling fluid or well service fluid in an amount sufficient to effect a reduction in the viscosity of said drilling fluid or well service fluid.

8. The method of claim 1 wherein said compound is added to said drilling fluid or well service fluid in an amount sufficient to maintain the flowability and pumpability of said drilling fluid or well service fluid at temperatures less than about 50 degrees Fahrenheit.

9. The method of claim 1 wherein said compound is added to said drilling fluid or well service fluid in quantities ranging from about 0.5 pounds to about 15.0 pounds of said compound per barrel of said drilling fluid or well service fluid.

10. The method of claim 1 wherein said compound reduces the viscosity of said

drilling fluid or well service fluid at low temperatures.

11. The method of claim 10 wherein said compound does not significantly affect the viscosity of said fluid at high temperatures.

12. The method of claim 1 wherein said compound is added to said fluid when said fluid is prepared.

13. The method of claim 1 wherein said compound is added to said fluid while said fluid is circulating in a wellbore.

14. A drilling fluid or well service fluid comprising a continuous oil phase, water dispersed in said oil phase, solids insoluble in said oil phase, and a compound having the formula:

$$R\text{-}(C_2H_4O)_n(C_3H_6O)_m(C_4H_7O)_k\text{-}H$$

where R is a saturated or unsaturated, linear or branched alkyl radical having about 8 to about 24 carbon atoms, n is a number ranging from about 1 to about 10, m is a number ranging from about 0 to about 10, and k is a number ranging from about 0 to about 10.

15. The drilling fluid or well service fluid of claim 14 wherein said compound is added in sufficient amounts to reduce the viscosity of said fluid at low temperatures.

16. The drilling fluid or well service fluid of claim 14 having a density of from about 8 to about 18 lbs/gal.

17. The drilling fluid or well service fluid of claim 14 having a yield point of not more than about 75 lbs/100 ft^2 at about 40°F.

18. A method of reducing the viscosity of an invert emulsion drilling fluid or well service fluid at low temperatures comprising adding to said fluid an effective amount of compound having the formula:

$$R-(C_2H_4O)_n(C_3H_6O)_m(C_4H_8O)_k-H$$

where R is a saturated or unsaturated, linear or branched alkyl radical having about 8 to about 24 carbon atoms, n is a number ranging from about 1 to about 10, m is a number ranging from about 0 to about 10, and k is a number ranging from about 0 to about 10.

19. The method of claim 18 wherein said compound does not significantly affect the viscosity of the drilling fluid at high temperatures.

20. The method of claim 18 further comprising circulating said fluid in a wellbore and adding said compound to said fluid during said circulation.

21. The method of claim 18 further comprising preparing said fluid and adding said compound to said fluid during said preparation.

Abstract

A method of reducing the viscosity of oil-based drilling fluids and well service fluids at low temperatures and a thinner compound for use in such drilling fluids and well service fluids is disclosed. The method comprises adding to said drilling fluids or well service fluids a thinner having the formula:

$$R\text{-}(C_2H_4O)_n(C_3H_6O)_m(C_4H_8O)_k\text{-}H$$

where R is a saturated or unsaturated, linear or branched alkyl radical having about 8 to about 24 carbon atoms, n is a number ranging from about 1 to about 10, m is a number ranging from about 0 to about 10, and k is a number ranging from about 0 to about 10.